MUNROE

The Effect of Ageing on the Iodine & Saponification Numbers of Chinese Wood Oil

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THE EFFECT OF AGEING ON THE IODINE AND SAPONIFICATION NUMBERS OF CHINESE WOOD OIL

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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THE EFFECT OF AGEING ON THE IODINE ABSORPTION AND SAPONIFICATION NUMBERS OF CHINESE WOOD OIL.

Chinese wood oil, also called tree oil, wood oil, or tung oil[74, 76, 77], comes from the seeds of Aluerites Cordata, the national tree of China and called by the Chinese, tung shu. It has a stately appearance, smooth green bark, and large spreading branches, which makes it one of the finest of shade trees. The tung shu flourishes in every province of the Yangsti valley, from the coast to the western part of the province of Szechuan. The fruits form a nut, in which three seeds, similar in shape to the Brazil nut, and having a hard and oleaginous kernel, are enclosed. The composition of the oil obtained from these seeds varies somewhat according to their source and the treatment given them in different localities.

This oil has been regarded by many observers as being practically identical with Japanese wood oil, and they have referred to the two indiscriminately under the designation "tung oil".[66]

Whilst resembling Chinese wood oil somewhat closely in its general characters, it appears to be chiefly obtained from the nuts of a different tree -viz., the Paulownia Imperialis, although it is not improbable that other seeds may be employed. Very little of this oil is exported from Japan, almost the whole output being required for home consumption. Its chief interest to the analyst lies in the fact that the two oils are not equally suitable for manufacturing purposes, and that accidental or intentional substitution of one for the other may occur.

TECHNOLOGY AND USES.

The method of extraction of the oil from the seed of the tung tree is a very crude one, and is very characteristically Chinese in every respect. The seeds are roasted in a flat dish over a naked fire until they are parched. They are then ground to a powder between stones. The mass is then expressed in crudely made wooden presses. The cold-drawn oil is pale yellow and is termed white tung oil. It is the variety chiefly exported. The oil obtained by hot pressing is dark brown and is termed black tung oil. This oil is chiefly consumed at home.[8] The yield amounts to only about 40 per cent of the weight of the nuts, although the kernels contain about 53 per cent.[76] The oil is allowed to settle, strained through coarse grass cloth, and is then ready for the market. It is sent down to Hankow, which is the chief shipping port, in large, wide-mouthed baskets, lined with putty and varnished paper. It is characterized by a very strong unpleasant odor.

Wood oil is used in China for lighting, as a varnish, for calking seams in ships, for manufacture of putty, and ink.[15, 76]

In this country and in Europe its consumption is steadily increasing. It is the most powerful drying oil known,[76] a thin film drying hard in 20 hours, whereas linseed oil requires 60 hours.[9] When heated to 500'F.(260'C.) for about 10 minutes, it gelatinizes. This change takes place very rapidly, and is probably due to a polymerization or a formation of inner anhydrides rather than to an oxidation.[9,13,16,66,71,75] Many attempts have been made to substitute Chinese wood oil for linseed oil in the manufacture of paints, and a number of patents have been taken out with this end in view, but thus far nothing has come of it. It has, however, been used in the manufacture of very high grade varnishes. It has also been used in the manufacture of a water-proof material, similar to oilcloth, but possessing an extraordinary degree of elasticity. In its gelatinized form it has been suggested that it might be used to a certain limited extent as a substitute for rubber, and as an insulating material.

HISTORICAL.

The earliest mention of Chinese wood oil found in the literature is in 1876,[22] when F.S.Cloëz noticed its peculiar properties and investigated "The nature of the fatty matter of the seed of the oil tree of China". In 1885 R.H.Davies[25] published an article on "Three Chinese fixed oils", one of which was the oil of the tung tree. Apparently nothing further was done with the oil until 1896. In August of that year W.H.Deering[9] studied the oil of the Chinese oil tree with especial reference to its saponification behaviour, and its property of gelatinizing. In 1897, in the United States Consular Report[18] a paragraph is given to this oil,-

the method of extraction, the tree and manner of growing. In the same year J.H.B.Jenkins[15] described the oil and gave some of its domestic uses. In 1897 the first patent[60] (English) relating to it appeared, followed by another in 1898 issued to the same people, proposing to use tung oil in the manufacture of varnishes,enamels, lacquers, etc. In 1898 J.H.B.Jenkins[69] contributed another article, giving some of the chemical constants, but it appears, in the light of more recent work, that he confused Chinese and Japanese wood oils. In 1898 A.Zucher,[61] writing on Chinese and Japanese wood oils, gave methods of preparation and a few constants. In 1901 F. Ulzer[62] attempted to deodorize Chinese wood oil, experimenting with alcohol, sodium bisulfite, animal charcoal and magnesium silicate, and superheated steam, but failed to get the desired effect. In January 1901 A.Kronstein[64] took out a patent for a process for thickening Chinese wood oil, and using the product as a substitute for hard resins. At the same time he took out another patent[63] for an improvement in oxidizing the oil, which did not seem to be very succesful. In 1901 L.E.Andès[65] published an article on the use of Chinese wood oil in the manufacture of body colour oils. In 1902 there appeared an anonymous article[10] on the manufacture of resins and varnishes from Chinese wood oil, and in the same year A. Henry[8] described the manufacture of the oil. M.Kitt,[16] in 1905 studied the gelatinization of tung oil, and concluded that it was due to the formation of inner anhydrides, and that the loss of weight which he noticed took place during the process was due to partial decomposition of the fat, and loss of glycerine. In the British Consular Report for 1908[46] W.D.Richardson describes the vegetable oils of China, touching on wood oil. A German patent was taken

out in 1908[48], to transform wood oil into a varnish-like, smooth, hard drying product, by heating it for a short time above the polymerization temperature, taking care to stir the mass constantly. Several articles relating to the determination of, or comments on, the constants of Chinese wood oil then appeared. These were by H. Blin[52], in 1909, A.Guiselin[51], E.W.Boughton[70], and A.Kreikenbaum[50] in 1910. The latter appears to be the first investigator who made a careful distinction between the Chinese and Japanese wood oils. This probably explains why the constants he gives are so consistent among themselves, and also why they vary from those given by others. In 1911 H.Gill and A.E.Shipee[54] studied methods for determining the unsaponifiable matter in wood oils. In the same year Dr.Wilhelm[55] wrote two papers on wood oil, discussing the constants, while A.H. Gill and A.E.Shipee[67] studied the liability of wood oils to gum on oxidation. In December 1912 A.Chester Chapman[66] published an article on the examination of Chinese wood oil. He appears to be the second man to differentiate closely and carefuly between Chinese and Japanese wood oil. As would be expected from this fact, the constants, which he gives, agree very closely with those given by Kreikenbaum in May 1910. He also goes into considerable detail in regard to special tests for qualitative estimation of the purity of the oil.(see 72.) In April 1912[73] a patent was taken out to prevent gelatinization of wood oil when heated, by boiling it with the naphthenic acids contained in the residues from refining the lighter petroleums. This year W.Fahrion[71] has four articles on a comparison of Chinese wood oil and linseed oil. He investigated

the nature of the fatty acids, and contradicts Cloëz[22]. Fahrion attempts to explain the gelatinization in two different ways,- one a molecular rearrangement through the action of light at ordinary temperatures; the other a polymerization, at a temperature of 150'C. or over. These give two different substances with different properties. W.Hoepfner and H.Burmeister[58] have investigated methods for examining Chinese wood oil. They used Hübl's method for determining the iodine number, and they also attempted to standardize the gelatinization of the oil.

The above resume represents all that has been found in the literature on Chinese wood oil. Much of this work is of little value because of the aforementioned confusion of the Chinese and Japanese oils.

As has been mentioned before, A.Kreikenbaum[50] was the first man to distinguish carefully between Chinese and Japanese wood oils, and it will be of value to us to consider his work more in detail. At the time of the publication of his article, dated March 11, 1910, Mr. Kreikenbaum was the chief chemist in the laboratories of the Glidden Varnish Company, in Cleveland, Ohio, and in this capacity he had access to large shipments of Chinese wood oil direct from China, the source of which was definitely known. Hence there was no opportunity for a confusion with the very similar Japanese wood oil. And for this reason the author says,- "The value of the work in this article and the results obtained and submitted in their entirety are due to the fact that the determinations of the constants have been made upon exact and carefully taken samples of Chinese wood oil". A summary of his re-

sults on the iodine and saponification values, together with the results obtained by Chapman, is shown in Table I. Mr. Kreikenbaum determined the iodine number by means of the Hübl standard method. The Hanus method was found to be inapplicable to Chinese wood oil, as it gave results different from those obtained by the Hübl method, and the results obtained were not consistent among themselves, varying from 191.2 to 212.8. In each case the solutions used were tested with a standard linseed oil, and gave good results.

OBJECT OF PRESENT WORK.

When Mr. Kreikenbaum had finished his work he sent the original samples to Prof. S.W.Parr of the University of Illinois, and since their arrival, nearly three years ago, they have been kept in the museum room of the chemical laboratory. Here they were exposed to the action of light (although some of the samples were contained in dark coloured bottles) and to variations in temperature from one season of the year to another in a steam heated room. They were also used for specimen samples in the class room, and from time to time the bottles were opened by students, who wished to compare the odor, colour and fluidity of the oil with other oils; and each time they were opened a fresh supply of air was admitted, taking with it a fresh supply of oxygen. These various factors would obviously have an effect on the properties of an oil, especially on as powerful a drying oil as Chinese wood oil. So it seemed worth while to determine the exact effect of ageing,- that is the combined effect of storage under these varying conditions,- on the iodine absorption and saponification numbers,- two of the most important constants of all oils.

TABLE I.

CHAPMAN'S RESULTS			KREIKENBAUM'S RESULTS		
Sample no.	Saponification no.	Iodine no.	Sample no.	Saponification no.	Iodine no.
1.	196.6	169.9	1.	191.9	170.2
2.	193.8	168.4	2.	190.6	170.6
3.	194.3	166.5	3.	191.8	170.3
4.	193.0	166.4	4.	190.7	170.4
5.	195.6	168.8	5.	191.3	172.8
6.	194.5	170.0	6.	191.8	170.1
7.	193.0	168.6	7.	190.6	170.1
8.	192.0	171.0	8.	189.9	170.7
9.	194.1	169.7	9.	190.6	171.6
10.	192.5	173.0	10.	190.6	171.6
11.	192.0	176.2	Average	190.9	170.4
12.	196.0	172.6			
13.	194.6	174.2			
14.	195.0	173.7			
15.	194.6	172.8			
16.	195.2	169.5			
17.	195.3	169.6			
Average	194.2	170.6			

In order to give a comparative value to the results which might be obtained, new samples of fresh Chinese wood oil were obtained, and the same determinations made on these as on the old samples, in the same way and under the same conditions. This opportunity is taken to acknowledge the courtesy of Marden, Orth, and Hastings, of Boston, Mass.; of Edward Hill's Son and Company, of New York; of G.W.S.Patterson and Company of New York; of L. C. Gillespie and Sons, of New York; and of Paterson, Boardman, and Knapp, of New York, who so very generously and promptly responded to the request for a representative sample of Chinese wood oil, and for information which would serve to identify the sample furnished; and also of the American Linseed Company, of South Chicago, Illinois, who furnished a sample of pure linseed oil.

EXPERIMENTAL WORK.

As explained above, two sets of samples were used in this work. First, the set of old samples which Mr. Kreikenbaum worked with in 1910, and second, a set of five samples of fresh oil, which were supplied by the aforementioned firms. These samples may be described as follows;-

Sample no.	Date	Age	Colour	Number of barrels taken from	Received from	Colour of bottle	Kind of stopper
1.	Oct.'08		light	100	Kreikenbaum	dark	cork
2.	" '07		"	100	"	"	"
4.	" "		"	20	"	"	"
5.	Sept."		dark	88	"	"	glass
7.	Oct.'08		light	100	"	"	cork
8.	June'09		"	249	"	light	"

Sample no.	Date	Age	Colour	Number of barrels taken from	Received from	Colour of bottle	Kind of stopper
9.	June'09		dark	200	Kreikenbaum	light	cork
10.	" "		"	500	"	"	"
100.	Mar.'13	7 mo	light	10	Patterson, Boardman & Knapp	dark	"
101.	" "	"	"	20	L.C.Gillespie & Sons	"	glass
102.	" "	"	"	300	G.W.S.Patterson & Co.	"	"
103.	" "	"	"	1	Edw. Hill's Son & Co.	"	"
104.	" "	"	"	100	Marden, Orth, and Hastings	"	cork
Linseed	May'13		raw		The Am Linseed Co.	light	"

Determination of the Iodine Absorption Number.

In the determination of the iodine number there was some question as to the method to use. Kreikenbaum used the Hübl method and showed the Hanus method to be inapplicable. Chapman used the Wijs method, and obtained results which agree very closely with those given by Kreikenbaum. But as the results of this work were to be compared directly with those given by Kreikenbaum, it was considered best to use the same method which he employed. The following proceedure was followed:- About 0.1 gram of oil was dissolved in 10-15 cc. of pure chloroform, and 25 cc. of the Hübl standard solution added,[78] and the reaction allowed to proceed 16-24 hours in the dark. The excess of iodine was then titrated with

a standard sodium thiosulphate solution. It was found that with this weight of oil and volume of reagent that there was more iodine left in the solution than there was absorbed by the oil, i.e., there was more than 100 per cent excess of iodine. Bartlett and Sherman,[1] Gantter,[2] Fahrien,[3] Sherman and Falk,[5] and Bremer[21] have all shown that it is necessary to have a large excess of iodine, at least as much in excess as is absorbed, in order to obtain a complete reaction and maximum absorption. The results of these determinations, together with the corresponding results obtained by Kreikenbaum on the same samples, and the value for the linseed oil are shown in Table II, on page 12.

Two variations were tried in the determination of the iodine number by Hübl's method. Ingle,[17] added the parts of the iodine solution, i.e., a solution of pure iodine in alclhol, and a solution of mercuric chloride in alcohol,- separately to the oil dissolved in chloroform, instead of mixing the two solutions and allowing the mixture to stand 6-8 hours before using. Inasmuch as the Hanus method was found to be inapplicable to Chinese wood oil, this variation in Hübl's method was tried:- About 0.1 gram of oil was dissolved in 10-15 cc. of chloroform, and then 15 cc. each of the solutions of iodine in alcohol and mercuric chloride in alcohol were added, and the reaction allowed to proceed 16-24 hours in the dark. The excess of iodine was titrated with the standard thiosulphate solution. The results obtained, together with these obtained by the standard method described above, are shown in Table III, on page 13.

The other variation in the method was in regard to the excess of iodine in the solution. A large enough sample of the

TABLE II.

Sample no.	Time hrs	Iodine Number			Max.	Min.	Av.	Kreikenbaum's	Dif.
1.	17½	167.2	166.8				167.0	170.2	3.2
2.	22½	163.4	163.2						
	16½	163.1	163.6		163.6	163.1	163.4	170.6	7.2
4.	18	165.2	165.3						
		165.7	165.4						
	17	165.3	165.2	165.6	165.7	165.2	165.4	170.4	5.0
5.	17½	170.2	168.0						
		171.0	170.3		171.0	168.0	169.9	172.8	2.9
7.	18	169.9	168.5	169.6	169.9	168.5	169.3	170.1	0.8
8.	18½	168.4	168.3						
	21		167.6		168.4	167.6	168.1	170.7	2.6
9.	18½	169.7	169.6						
	21		168.2		169.7	168.2	169.2	171.6	2.4
10.	20	169.4	168.8	168.5					
	18½	169.5	170.3	170.3	170.3	168.5	169.5	171.6	2.1
100.	20	169.8	170.3						
		169.5	171.1		171.1	169.5	170.2		
101.	27½	170.7	170.9						
	19	171.1	170.6	170.7	171.1	170.7	170.8		
102.	28½	170.5	171.6	171.5	171.6	170.5	171.2		
103.	19	169.9	169.8	170.3	170.3	169.8	170.0		
104.	29	169.4	171.6						
	19		169.6		171.6	169.4	170.2		
Linseed	7	191.4	191.6				191.5		

TABLE III.

SOLUTIONS ADDED SEPARATELY.

Sample no.	Time in hours	Iodine Number		Average	Values by the standard method
2.	21	159.9	167.7	163.8	163.4
2.	6	159.9	160.8	160.4	"
2.	48	162.6	163.0	162.8	"
2.	21	159.3	142.0	150.6	"
4.	23	165.9	165.9	165.9	165.4
4.	6½	156.8	157.9	157.4	"
4.	26½	159.8	159.9	159.9	"
4.	67	152.3	153.3	152.8	"
4.	67	153.6	150.8		
		151.5	154.3		
		149.3	152.9	152.1	"
5.	27	164.6	164.2	164.4	169.9

oil was taken so that with 25 cc. of Hübl's atandard solution there would be more iodine absorbed than there was left in excess, i.e., there was less than 100 per cent excess of iodine. These results, together with the values obtained with the standard method, using more than 100 per cent excess of iodine, are shown in Table IV, on page 15.

The relation between time and iodine absorption was then determined. A number of determinations were made on the same oil, using the same solutions, but allowing the absorption to proceed for different lengths of time. This was done with both a sample of the Chinese wood oil, and also the linseed oil. These results are shown in Table V, on page 15, and also graphically in Plate I, on page 16.

Determination of the Saponification Number.

The saponification number was determined in the following manner:- About 2.0 grams of oil were treated with about 20 cc. of approximately 0.6 N. alcoholic KOH solution, and, with a reflux condenser attached to the flask, the mixture was heated for about half an hour on the steam bath. The excess of KOH was titrated with an accurately standardized HCl solution. At the same time the strength of the KOH solution was determined by titrating it alone with the HCl. This gave the acid in terms of the alkali, and the normality of the KOH solution could then be calculated. The results obtained, together with the corresponding results obtained by Kreikenbaum, and the value for the linseed oil, are shown in Table VI, on page 17.

Determination of the Refractive Index.

The refractive index was determined with an Abbè Refrac-

TABLE IV.

LESS THAN 100 PER CENT IODINE.

Sample no.	Time hrs.	Iodine Number			Average	Values by standard method
2.	21½	178.8	175.6	169.2	174.5	163.4
2.	21	178.8	169.2	175.6	174.5	"
2.	27½	159.1	161.0		159.6	"
2.	6	159.9	160.8		160.4	"
8.	19½	169.9	180.2	158.3	166.1	168.1
9.	19	178.8	177.9	176.4	177.7	169.2
10.	18	167.6	164.9	161.4	164.6	169.5
10.	6	165.8	163.8		164.8	"

TABLE V.

RELATION BETWEEN TIME AND ABSORPTION.

Sample no.	Time in hours	Iodine Number			Average
4.	1	151.0	151.2		151.1
4.	3	159.0	161.4		159.7
4.	5	161.9	162.1		162.0
4.	6½	163.1	163.3		163.2
4.	17	165.3	165.2	165.6	165.4
Linseed	1	181.7	182.3		182.0
"	3	190.3	189.7		190.0
"	5	190.9	191.3		191.1
"	7	191.1	191.6		191.5

PLATE I

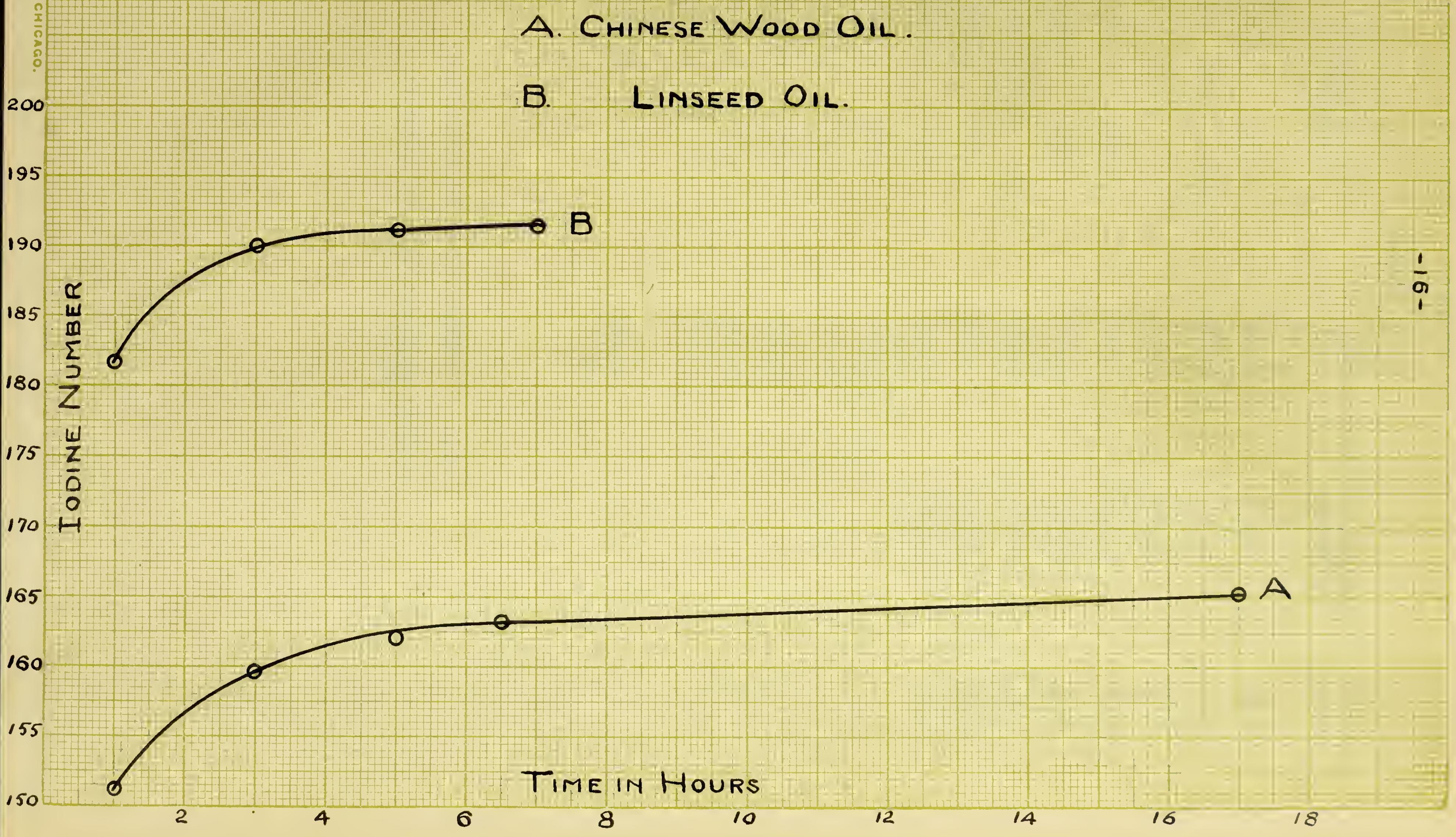
A. CHINESE WOOD OIL.
B. LINSEED OIL.
B
A
IODINE NUMBER
200
195
190
185
180
175
170
165
160
155
150
TIME IN HOURS
2
4
6
8
10
12
14
16
18

TABLE VI.

Sample no.	Saponification Number			Average	Kreikenbaum's Results	Difference
1.	192.3	192.7		192.5	191.9	0.6
2.	194.5	194.8	194.5	194.6	190.6	4.0
4.	194.1	195.1	195.5	194.9	190.7	4.2
5.	195.7	195.7		195.7	191.3	4.4
7.	195.7	195.7		195.7	190.6	5.1
8.	195.5	195.5	194.7	195.2	189.9	5.3
9.	192.6	191.4		192.0	190.6	1.4
10.	192.2	192.1		192.2	190.6	1.6
100.	190.7	189.9		190.3		
101.	189.9	190.0		190.0		
102.	190.7	190.9		190.8		
103.	191.5	191.4		191.5		
104.	191.4	190.1		190.7		
Linseed Oil	187.7	187.3		187.5		

AVERAGE OF OLD SAMPLES 194.1

AVERAGE OF NEW SAMPLES 190.6

tometer, manufactured by Carl Zeiss. This determination was made upon the old samples, the new samples, and the sample of linseed oil. The results are shown in Table VII, on page 19.

RESUME AND CONCLUSIONS.

Briefly then, the iodine and saponification numbers, as representing the two most important constants of an oil, and also the two which would be likely to be affected the most by ageing, were determined on a set of eight old samples of Chinese wood oil, the origin of which was definitely known. These values were compared with the same values the oil had when it was fresh, and also with the same constants of a set of five samples of fresh, pure Chinese wood oil, and with the same values of a sample of pure linseed oil. The conclusions which may be drawn from the work done and the results obtained are as follows:-

I. Ageing, under the conditions of this experiment, lowers the iodine number. This decrease in the iodine value may be explained by assuming that the slow oxidation, which the oil is subjected to, partially saturates some of the unsaturated hydro-carbons, leaving fewer points of attack for the iodine, and thus decreasing the amount of iodine taken up.

II. The method of Ingle in determining the iodine number, i.e., adding the parts of the iodine solution separately to the oil dissolved in chloroform, does not seem to be applicable to Chinese wood oil. The results obtained by this method vary from those obtained by the standard method, and they also vary considerably among themselves.

THE REFRACTIVE INDEX.

Sample no.	Refractive index
1.	1.5175
2.	1.5176
4.	1.5178
5.	1.5170
7.	1.5173
8.	1.5172
9.	1.5171
10.	1.5171
100.	1.5169
101.	1.5169
102.	1.5168
103.	1.5168
Linseed oil	1.4805

III. It is also shown that in order to get results which are consistent, there must be present in the solution at least as much iodine in excess as there is absorbed by the oil. This is quite in accordance with the work of Bartlett and Sherman, Gantter, Fahrion, Sherman and Falk, and Bremer.

IV. As can readily be seen from the curve on Plate I., the absorption proceeds very rapidly from the start, and is not complete until after about 14 hours. This is quite different from the behaviour of the linseed oil. Although it has a higher iodine number, it is seen that the absorption proceeds much more rapidly, and is complete in 5-7 hours.

V. Ageing raises the saponification number. This increase is probably due to the decomposition of the fatty acids into other acids with a smaller number of carbon atoms, but having in the aggregate a larger number of carboxyl groups, which present more points of attack for the action of the alkali.

VI. We are led to conclude that the mere fact of variation of the iodine and saponification numbers from the standard values ordinarily accepted, does not conclusively prove that the oil has been adulterated, since the above results show that the constants of an oil may change as a result of ageing. But by the determination of several constants for the same oil, and by knowing the different effects of age and adulteration on these constants, it would be possible to draw correct conclusions as to the purity of the sample, even if this ageing has taken place.

VII. By considering together the results obtained by Kreikenbaum,

by Chapman, and those obtained in this work on the new samples, one can see how uniform a product is the Chinese wood oil of commerce. Kreikenbaum pointed out this fact from his own results.

It is interesting to compare the results of this work with those obtained by Marshall and Ryan[43]. In 1907 they investigated, among other things, the influence of oxygen on the iodine and saponification numbers of olive oil. They found that the action of the oxygen was to lower the iodine number, and to raise the saponification number.

The refractive index of these oils was determined, not because this determination was of any immediate value in connection with this work, but because it was hoped that in the future this work would be continued along the lines of this investigation, taking up the effect of ageing on the other constants, and, since Kreikenbaum did not give those values, it was thought best to make these determinations for future reference. It would be of value and of interest if the exact influence of time alone could be determined, and also how this varies from year to year or from month to month. And if this work would be continued, taking up the effect of ageing on the specific gravity, the viscosity, the heat of bromination, the acetyl value, the refractive index, the Maumené value, and the point of solidification, or rather polymerization, a long step will have been taken in assisting the analyst in determining whether a sample of oil is pure.

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